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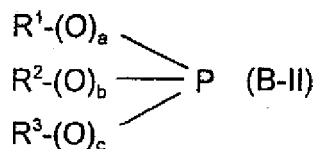
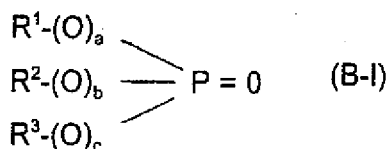
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(54) Title: LUBRICATING OIL COMPOSITION



(57) Abstract: This invention relates to a lubricating oil composition, comprising (A) a base oil; and a phosphorus-containing compound represented by the formulae (B-I) or (B-II): wherein in Formulae (B-I) and (B-II), R¹, R² and R³ are independently hydrogen or hydrocarbyl groups, and a, b and c are independently zero or 1; the lubricating oil composition being characterized by a sulfur content of 0.01 to 0.25 % by weight.

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TITLE: LUBRICATING OIL COMPOSITION**Technical Field**

This invention relates to lubricating oil compositions. More particularly, this invention relates to lubricating oil compositions containing relatively low levels of sulfur.

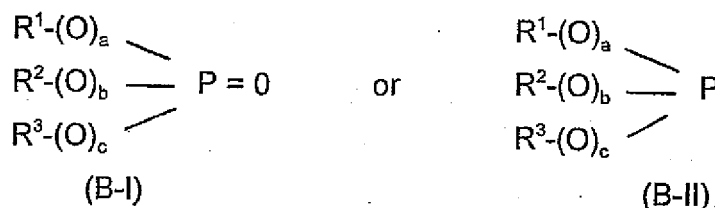
Background of the Invention

In the ever-increasing effort to reduce exhaust gas emissions from internal combustion engines, manufacturers of gasoline powered engines and diesel engines are turning more and more to using exhaust gas after treatment devices (e.g., catalytic converters, particulate traps, etc.) to reduce emissions. A problem with using such devices, however, is that lubricating oil compositions containing relatively high levels of sulfur eventually decompose and the decomposition products of these lubricants, including the sulfur, eventually enter the aftertreatment device and often contribute to damaging the device. Additionally, the allowable level of sulfur in diesel and gasoline fuels is expected to drop to 15 parts per million (ppm) with zero-sulfur fuel already being required in select locations. Therefore, a substantial portion of the sulfur in the emissions of these engines can be expected to be attributed to sulfur in the lubricant. This has resulted in pressure to reduce sulfur levels in the lubricating oil compositions used in these engines.

The present invention provides a solution to this problem by providing lubricating oil compositions containing relatively low levels of sulfur.

Summary of the Invention

This invention relates to a lubricating oil composition, comprising: (A) a base oil; and (B) a phosphorus-containing compound represented by the formulae



wherein in Formulae (B-I) and (B-II), R^1 , R^2 and R^3 are independently hydrogen or hydrocarbyl groups, and a, b and c are independently zero or 1; the lubricating oil composition being characterized by a sulfur content of 0.01 to 0.25% by weight. In one embodiment, the lubricating oil composition further comprises (C) an acylated nitrogen-containing compound having a substituent of at least 10 aliphatic carbon atoms, (D) an alkali or alkaline earth metal salt of an organic sulfur acid, a carboxylic acid or a phenol; (E) an alkali or alkaline earth metal salt of a hydrocarbon-substituted saligenin; (F) a metal salt of a phosphorus-containing compound; (G) a dispersant viscosity index modifier; or (H) one or more additional optional additives. The inventive composition may be made by blending components (A) and (B), and optionally one or more of components (C) to (H), using known blending techniques and any order of mixing or addition.

Description of the Preferred Embodiments

The term "hydrocarbyl" denotes a group having a carbon atom directly attached to the remainder of the molecule and having a hydrocarbon or predominantly hydrocarbon character within the context of this invention. Such groups include the following:

(1) Purely hydrocarbon groups; that is, aliphatic, alicyclic, aromatic, aliphatic- and alicyclic-substituted aromatic, aromatic-substituted aliphatic and alicyclic groups, and the like, as well as cyclic groups wherein the ring is completed through another portion of the molecule (that is, any two indicated substituents may together form an alicyclic group). Examples include methyl, ethyl, cyclohexyl, phenyl, etc.

(2) Substituted hydrocarbon groups; that is, groups containing non-hydrocarbon substituents which do not alter the predominantly hydrocarbon character of the group. Examples include hydroxy, nitro, cyano, alkoxy, acyl, etc.

(3) Hetero groups; that is, groups which, while predominantly hydrocarbon in character, contain atoms other than carbon in a chain or ring otherwise composed of carbon atoms. Suitable hetero atoms include nitrogen, oxygen and sulfur.

In general, no more than three substituents or hetero atoms, and typically no more than one, will be present for each 10 carbon atoms in the hydrocarbyl group.

The terms "hydrocarbon" and "hydrocarbon-based" have the same meaning and can be used interchangeably with the term hydrocarbyl when referring to molecular groups having a carbon atom attached directly to the remainder of a molecule.

The term "lower" as used herein in conjunction with terms such as hydrocarbyl, alkyl, alkenyl, alkoxy, and the like, is intended to describe such groups which contain a total of up to 7 carbon atoms.

The term "oil-soluble" refers to a material that is soluble in mineral oil to the extent of at least one gram per liter at 25°C.

The term "TBN" refers to total base number. This is the amount of acid (perchloric or hydrochloric) needed to neutralize all or part of a material's basicity, expressed as milligrams of KOH per gram of sample.

The Lubricating Oil Composition.

The inventive lubricating oil composition is comprised of one or more base oils which are generally present in a major amount. The base oil may be present in an amount greater than 60%, or greater than 70%, or greater than 75% by weight of the lubricating oil composition.

The inventive lubricating oil composition may have a viscosity of up to 16.3 cSt at 100°C, and in one embodiment 5 to 16.3 cSt at 100°C, and in one embodiment 6 to 13 cSt at 100°C.

The inventive lubricating oil composition may have an SAE Viscosity Grade of 0W, 0W-20, 0W-30, 0W-40, 0W-50, 0W-60, 5W, 5W-20, 5W-30, 5W-40, 5W-50, 5W-60, 10W, 10W-20, 10W-30, 10W-40 or 10W-50.

The inventive lubricating oil composition is characterized by a sulfur content of 0.01 to 0.25% by weight, and in one embodiment 0.05 to 0.25%, and in one embodiment 0.10 to 0.25% by weight, and in one embodiment 0.01 to 0.20% by weight, and in one embodiment 0.01 to 0.15% by weight.

The inventive lubricating oil composition is characterized by a phosphorus content in the range of 0.02 to 0.14% by weight, and in one embodiment 0.05 to 0.14% by weight, and in one embodiment 0.08 to 0.14% by weight, and in one embodiment 0.10 to 0.14% by weight.

The ash content of the inventive lubricating oil composition as determined by the procedures in ASTM D-874-96 may be in the range of 0.3 to 1.4% by weight, and in one embodiment 0.3 to 1.2% by weight, and in one embodiment 0.3 to 1.1% by weight, and in one embodiment 0.5 to 1.1% by weight.

In one embodiment, the inventive lubricating oil composition is characterized by a chlorine content of up to 100 ppm, and in one embodiment up to 50 ppm, and in one embodiment up to 10 ppm.

The inventive lubricating oil compositions are characterized by reduced sulfur levels when compared to those in the prior art, and yet, at least in one embodiment, exhibit antiwear properties that are sufficient to pass industry standard tests for antiwear.

(A) The Base Oil

The base oil used in the inventive lubricating oil composition may be selected from any of the base oils in Groups I-V as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. The five base oil groups are as follows:

<u>Base Oil Category</u>	<u>Sulfur (%)</u>		<u>Saturates(%)</u>	<u>Viscosity Index</u>
Group I	>0.03	and/or	<90	80 to 120
Group II	≤0.03	and	≥90	80 to 120
Group III	≤0.03	and	≥90	≥120
Group IV	All polyalphaolefins (PAOs)			
Group V	All others not included in Groups I, II, III or IV			

Groups I, II and III are mineral oil base stocks.

The base oil may be a natural oil, synthetic oil or mixture thereof, provided the sulfur level in such base oil is sufficiently low enough so that the sulfur level in the

inventive lubricating oil composition does not exceed the above indicated concentration level required for the inventive lubricating oil composition. The natural oils include animal oils and vegetable oils (e.g., castor oil, lard oil) as well as mineral lubricating oils such as liquid petroleum oils and solvent treated or acid-treated mineral lubricating oils of the paraffinic, naphthenic or mixed paraffinic-naphthenic types. Oils derived from coal or shale are also useful.

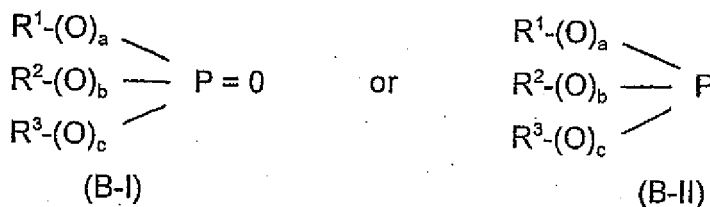
Synthetic oils include hydrocarbon oils such as polymerized and interpolymers of olefins, alkylbenzenes, polyphenyls, alkylated diphenyl ethers, alkylated diphenyl sulfides, and derivatives, analogs and homologs thereof. The synthetic oils include alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc.; esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids, alkenyl succinic acids, etc.) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, etc.); and esters made from C₅ to C₁₂ monocarboxylic acids and polyols or polyol ethers.

The base oil may be a polyalphaolefin (PAO) or an oil derived from Fischer-Tropsch synthesized hydrocarbons.

Unrefined, refined and rerefined oils, either natural or synthetic (as well as mixtures of two or more of any of these) of the type disclosed hereinabove can be used as the base oil.

(B) Phosphorus-Containing Compound

The phosphorus-containing compound (B) is a compound represented by the formulae



wherein in Formulae (B-I) and (B-II), R^1 , R^2 and R^3 are independently hydrogen or hydrocarbyl groups, and a, b and c are independently zero or 1. The phosphorus-containing compound (B) can be a phosphate, phosphonate, phosphinate or phosphine oxide. The phosphorus-containing compound (B) can be a phosphite, phosphonite, phosphinite or phosphine. The phosphorus-containing compound can be a mixture of two or more of any of the foregoing.

The total number of carbon atoms in R^1 , R^2 and R^3 in Formulae (B-I) and (B-II) must be sufficient to render the compound soluble in the base oil (A). Generally, the total number of carbon atoms in R^1 , R^2 and R^3 is at least 8, and in one embodiment at least 12. There is no limit to the total number of carbon atoms in R^1 , R^2 and R^3 that is required, but a practical upper limit is 400 or 500 carbon atoms. Each R^1 , R^2 and R^3 may be the same as the other, although they may be different. Examples of useful R^1 , R^2 and R^3 groups include isopropyl, n-butyl, isobutyl, amyl, 4-methyl-2-pentyl, isooctyl, decyl, dodecyl, tetradecyl, 2-pentenyl, dodecenyl, phenyl, naphthyl, alkylphenyl, alkylnaphthyl, phenylalkyl, naphthylalkyl, alkylphenylalkyl, alkylnaphthylalkyl, and the like. In one embodiment, the phosphorus-containing compound (B) is represented by the Formula (B-I) wherein each R^1 , R^2 and R^3 is an alkyl aromatic (e.g., alkyl phenyl) group, and a, b and c are each 1. In one embodiment, the phosphorus-containing compound (B) is represented by the Formula (B-II) wherein each R^1 , R^2 and R^3 is an aromatic (e.g., phenyl) group, and a, b and c are each 1.

The phosphorus compounds represented by Formulae (B-I) and (B-II) can be prepared by reacting a phosphorus acid or anhydride with an alcohol or mixture of alcohols corresponding to R^1 , R^2 and R^3 in Formulae (B-I) or (B-II). The phosphorus acid or anhydride is generally an inorganic phosphorus reagent such as phosphorus pentoxide, phosphorus trioxide, phosphorus tetraoxide, phosphorus acid, phosphorus halide, or lower phosphorus esters, and the like. Lower phosphorus acid esters contain from 1 to 7 carbon atoms in each ester group. The phosphorus acid ester may be a mono, di- or triphosphoric acid ester.

A useful phosphorus-containing compound is available from FMC under the trade designation Durad 310M which is identified as a tri (alkyl phenol) phosphate. Another useful compound is triphenyl phosphite.

5 The phosphorus-containing compound (B) may be employed in the inventive lubricating oil composition at a concentration in the range of 0.2 to 1.5% percent by weight, and in one embodiment 0.4% to 1% by weight, and in one embodiment 0.5 to 0.8% by weight.

(C) Acylated Nitrogen-Containing Compound

10 In one embodiment, the inventive lubricating oil composition further comprises an acylated nitrogen-containing compound having a substituent of at least 10 aliphatic carbon atoms. These compounds typically function as ashless dispersants.

15 A number of acylated, nitrogen-containing compounds having a substituent of at least 10 aliphatic carbon atoms and made by reacting a carboxylic acid acylating agent with an amino compound are known to those skilled in the art. In such compositions the acylating agent is linked to the amino compound through an imido, amido, amidine or salt linkage. The substituent of at least 10 aliphatic carbon atoms may be in either the carboxylic acid acylating agent derived portion of the molecule or in the amino compound derived portion of the molecule.

20 Illustrative hydrocarbon based groups containing at least 10 carbon atoms are n-decyl, n-dodecyl, tetrapropylene, n-octadecyl, oleyl, chlorooctadecyl, tricontanyl, etc. Generally, the hydrocarbon-based substituents are made from homo- or interpolymers (e.g., copolymers, terpolymers) of mono- and di-olefins having 2 to 10 carbon atoms, such as ethylene, propylene, 1-butene, isobutene, butadiene, isoprene, 1-hexene, 1-octene, etc. Typically, these olefins are 1-monoolefins. The
25 substituent can also be derived from the halogenated (e.g., chlorinated or brominated) analogs of such homo- or interpolymers.

A useful source of the hydrocarbon-based substituents are poly(isobutene)s obtained by polymerization of a C₄ refinery stream having a butene content of 35 to 75 weight percent and isobutene content of 30 to 60 weight percent in the presence

of a Lewis acid catalyst such as aluminum trichloride or boron trifluoride. These polybutenes contain predominantly isobutene repeating units.

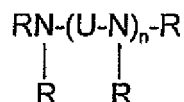
In one embodiment, the substituent is a polyisobutene group derived from a polyisobutene having a high methylvinylidene isomer content, that is, at least 70% methylvinylidene, and in one embodiment at least 80% methylvinylidene. Suitable high methylvinylidene polyisobutenes include those prepared using boron trifluoride catalysts.

The acylating agent or reagent can vary from formic acid and its acyl derivatives to acylating agents having high molecular weight aliphatic substituents of up to 5,000, 10,000 or 20,000 carbon atoms. In one embodiment, the acylating agent is a hydrocarbon substituted succinic acid or anhydride containing hydrocarbon-based substituent groups and succinic groups wherein the substituent groups are derived from a polyalkene such as polyisobutene. The acid or anhydride may be characterized by the presence within its structure of an average of at least 0.9 succinic group for each equivalent weight of substituent groups, and in one embodiment 0.9 to 2.5 succinic groups for each equivalent weight of substituent groups. The polyalkene generally has number average molecular weight (\bar{M}_n) of at least 700, and in one embodiment 700 to 2000, and in one embodiment 900 to 1800. The ratio between the weight average molecular weight (\bar{M}_w) and the (\bar{M}_n) (that is, the \bar{M}_w/\bar{M}_n) can range from 1 to 10, and in one embodiment 1.5 to 5, and in one embodiment 2.5 to 5. For purposes of this invention, the number of equivalent weights of substituent groups is deemed to be the number corresponding to the quotient obtained by dividing the \bar{M}_n value of the polyalkene from which the substituent is derived into the total weight of the substituent groups present in the substituted succinic acid.

The amino compound may be characterized by the presence within its structure of at least one $\text{HN}<$ group and can be a monoamine or polyamine. Mixtures of two or more amino compounds can be used in the reaction with one or more acylating reagents. In one embodiment, the amino compound contains at least

one primary amino group (i.e., -NH_2). In one embodiment, the amine is a polyamine, for example, a polyamine containing at least two -NH- groups, either or both of which are primary or secondary amines. The amines may be aliphatic, cycloaliphatic, aromatic or heterocyclic amines. Hydroxy substituted amines, such as alkanol amines (e.g., mono- or diethanol amine) and hydroxy (polyhydrocarbyloxy) analogs of such alkanol amines, may be used.

Among the useful amines are the alkylene polyamines, including the polyalkylene polyamines. The alkylene polyamines include those conforming to the formula



wherein n is from 1 to 14; each R is independently a hydrogen atom, a hydrocarbyl group or a hydroxy-substituted or amine-substituted hydrocarbyl group having up to 30 atoms, or two R groups on different nitrogen atoms can be joined together to form a U group, with the proviso that at least one R group is a hydrogen atom and U is an alkylene group of 2 to 10 carbon atoms. U may be ethylene or propylene. Alkylene polyamines where each R is hydrogen or an amino-substituted hydrocarbyl group with the ethylene polyamines and mixtures of ethylene polyamines are useful. Usually n will have an average value of from 2 to 10. Such alkylene polyamines include methylene polyamine, ethylene polyamines, propylene polyamines, butylene polyamines, pentylene polyamines, hexylene polyamines, heptylene polyamines, etc. The higher homologs of such amines and related amino alkyl-substituted piperazines are also included.

Alkylene polyamines that are useful include ethylene diamine, diethylene triamine, triethylene tetramine, propylene diamine, trimethylene diamine, hexamethylene diamine, decamethylene diamine, octamethylene diamine, di(heptamethylene) triamine, tripropylene tetramine, tetraethylene pentamine, trimethylene diamine, pentaethylene hexamine, di(trimethylene)triamine, N-(2-

aminoethyl)piperazine, 1,4-bis(2-aminoethyl)piperazine, and the like. Higher homologs as are obtained by condensing two or more of the above-illustrated alkylene amines are useful, as are mixtures of two or more of any of the afore-described polyamines.

5 Useful polyamines are those resulting from stripping polyamine mixtures. In this instance, lower molecular weight polyamines and volatile contaminants are removed from an alkylene polyamine mixture to leave as residue what is often termed "polyamine bottoms". In general, alkylene polyamine bottoms can be characterized as having less than 2% by weight, usually less than 1% by weight
10 material boiling below 200°C.

 The acylated nitrogen-containing compounds include amine salts, amides, imides, amidines, amidic acids, amidic salts and imidazolines as well as mixtures thereof. To prepare the acylated nitrogen-containing compounds from the acylating reagents and the amino compounds, one or more acylating reagents and one or
15 more amino compounds are heated, optionally in the presence of a normally liquid, substantially inert organic liquid solvent/diluent, at temperatures in the range of 80°C up to the decomposition point of either the reactants or the carboxylic derivative but normally at temperatures in the range of 100°C up to 300°C, provided 300°C does not exceed the decomposition point. Temperatures of 125°C to 250°C are normally
20 used. The acylating reagent and the amino compound are reacted in amounts sufficient to provide from one-half equivalent up to 2 moles of amino compound per equivalent of acylating reagent.

 The acylated nitrogen-containing compound (C) may be employed in the inventive lubricating oil composition at a concentration in the range of up to 10% by weight, and in one embodiment 1 to 10% percent by weight, and in one embodiment
25 2% to 5% by weight.

(D) Alkali or Alkaline Earth Metal Salt of Organic Sulfur Acid, Carboxylic Acid, Lactone or Phenol

The alkali metal or alkaline earth metal salts (D) are salts of organic sulfur acids, carboxylic acids, lactones or phenols. These salts may be neutral or overbased. The former contain an amount of metal cation just sufficient to neutralize the acidic groups present in the salt anion; the latter contain an excess of metal cation and are often termed basic, hyperbased or superbased salts.

The organic sulfur acids are oil-soluble organic sulfur acids such as sulfonic, sulfamic, thiosulfonic, sulfinic, sulfenic, partial ester sulfuric, sulfurous and thiosulfuric acid. Generally they are salts of aliphatic or aromatic sulfonic acids. The sulfonic acids include the mono- or poly-nuclear aromatic or cycloaliphatic compounds.

The carboxylic acids include aliphatic, cycloaliphatic, and aromatic mono- and polybasic carboxylic acids such as the naphthenic acids, alkyl- or alkenyl-substituted cyclopentanoic acids, alkyl- or alkenyl-substituted cyclohexanoic acids, alkyl- or alkenyl-substituted aromatic carboxylic acids. The aliphatic acids generally contain at least 8 carbon atoms, and in one embodiment at least 12 carbon atoms. Usually they have no more than 400 carbon atoms. The cycloaliphatic and aliphatic carboxylic acids can be saturated or unsaturated.

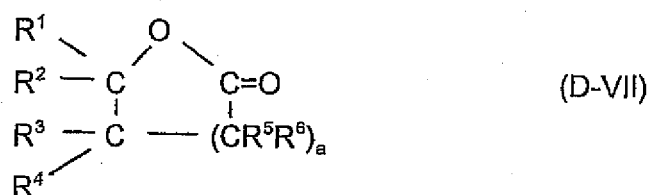
A useful group of carboxylic acids are the oil-soluble aromatic carboxylic acids. These acids are represented by the formula:



wherein in Formula (D-III), R^* is an aliphatic hydrocarbon-based group of 4 to 400 aliphatic carbon atoms, a is an integer of from one to four, Ar^* is a polyvalent aromatic hydrocarbon nucleus of up to 14 carbon atoms, each X is independently a sulfur or oxygen atom, and m is an integer of from one to four with the proviso that R^* and a are such that there is an average of at least 8 aliphatic carbon atoms provided by the R^* groups for each acid molecule represented by Formula (D-III).

A useful group of carboxylic acids are the aliphatic-hydrocarbon substituted salicylic acids wherein each aliphatic hydrocarbon substituent contains an average of at least 8 carbon atoms, and in one embodiment at least 16 carbon atoms per substituent, and the acids contain one to three substituents per molecule. A useful aliphatic-hydrocarbon substituted salicylic acid is C₁₆-C₁₈ alkyl salicylic acid.

A group of carboxylic acid derivatives that are useful are the lactones represented by the formula



wherein in Formula (D-VII), R¹, R², R³, R⁴, R⁵ and R⁶ are independently H, hydrocarbyl groups or hydroxy substituted hydrocarbyl groups of from 1 to 30 carbon atoms, with the proviso that the total number of carbon atoms must be sufficient to render the lactones oil soluble; R² and R³ can be linked together to form an aliphatic or aromatic ring; and a is a number in the range of zero to 4. A useful lactone can be prepared by reacting an alkyl (e.g., dodecyl) phenol with glyoxylic acid at a molar ratio of 2:1.

Neutral and basic salts of phenols (generally known as phenates) are also useful in the compositions of this invention and well known to those skilled in the art. The phenols from which these phenates are formed are of the general formula



wherein in Formula (D-IX), R*, a, Ar*, and m have the same meaning as described hereinabove with reference to Formula (D-III).

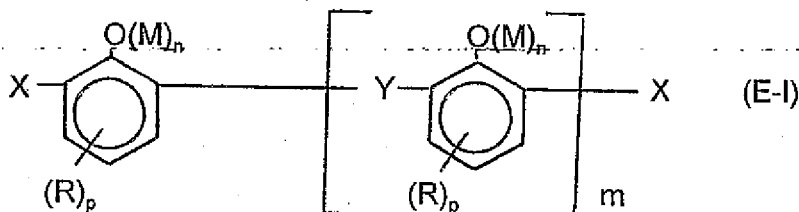
Mixtures of two or more neutral and basic salts of the hereinabove described organic sulfur acids, carboxylic acids and phenols can be used in the compositions of this invention.

The alkali and alkaline earth metals that are useful include sodium, potassium, lithium, calcium, magnesium, strontium and barium, with calcium and magnesium being especially useful.

The metal salt (D) may be employed in the inventive lubricating oil composition at a concentration in the range of up to 5% by weight, and in one embodiment 0.5 to 5% percent by weight, and in one embodiment 1% to 2.5% by weight.

(E) Alkali or Alkaline Earth Metal Salt of a Hydrocarbon-Substituted Saligenin

The alkali or alkaline earth metal salt of a hydrocarbon-substituted saligenin may be a compound represented by the formula



wherein in Formula (E-I): each X independently is -CHO or -CH₂OH; each Y independently is -CH₂- or -CH₂OCH₂-; wherein the -CHO groups comprise at least 10 mole percent of the X and Y groups; each M is independently a valence of an alkali or alkaline earth metal ion; each R is independently a hydrocarbyl group containing 1 to 60 carbon atoms; m is 0 to 10; n is 0 or 1 provided that when n is 0 the M is replaced with H; and each p is independently 0, 1, 2, or 3; provided that at least one aromatic ring contains an R substituent and that the total number of carbon atoms in all R groups is at least 7; and further provided that if m is 1 or greater, then one of the X groups can be -H.

The alkali and alkaline earth metals that are useful include sodium, potassium, lithium, calcium, magnesium, strontium and barium, with calcium and magnesium

being especially useful. In Formula (E-I), when the metal M is a divalent metal (e.g., calcium or magnesium) the other valence of M, not shown, may be satisfied by other anions or by association with an additional -O⁻ functionality of the same saligenin derivative.

5 In Formula (E-I), each n is independently 0 or 1, provided that when n is 0, the M is replaced by H, that is, to form an unneutralized phenolic -OH group. The average value of n is typically 0.1 to 1.0. In one embodiment, m is 2 to 9, and in one embodiment 3 to 8, and in one embodiment 4 to 6.

10 Most of the aromatic rings in Formula (E-I) contain at least one R substituent, which is a hydrocarbonyl group, and in one embodiment an alkyl group, containing 1 to 60 carbon atoms, and in one embodiment 7 to 28 carbon atoms, and in one embodiment 9 to 18 carbon atoms. R can be linear or branched. Each aromatic ring in the structure may be substituted with 0, 1, 2, or 3 such R groups (that is, p is 0, 1, 2, or 3), most typically 1. Different rings in a given molecule may contain different
15 numbers of such substituents. At least one aromatic ring in the molecule must contain at least one R group, and the total number of carbon atoms in all the R groups in the molecule should be at least 7, and in one embodiment at least 12.

20 In Formula (E-I), the X and Y groups may be seen as groups derived from formaldehyde or a formaldehyde source, by condensative reaction with the aromatic molecule. While various species of X and Y may be present, the commonest species comprising X are -CHO (aldehyde functionality) and -CH₂OH (hydroxymethyl functionality); similarly the commonest species comprising Y are -CH₂- (methylene bridge) and -CH₂OCH₂- (ether bridge).

25 The relative amounts of the various X and Y groups depends to a certain extent on the conditions of synthesis of the molecules. Under many conditions the amount of -CH₂OCH₂- groups is relatively small compared to the other groups and is reasonably constant at 13 to 17 mole percent. Ignoring the amount of such ether groups and focusing on the relative amounts of the -CHO, -CH₂OH, and -CH₂-

groups, useful compositions have the following relative amounts of these three groups, the total of such amounts in each case being normalized to equal 100%:

-CHO:	15-100%	or	20-60%	or	25-50%
-CH ₂ OH:	0-54%	or	4-46%	or	10-40%
-CH ₂ -:	0-64%	or	18-64%	or	20-60%

The compound represented by Formula (E-I) may be a magnesium salt, and the presence of magnesium during the preparation of the compound is believed to be important in achieving the desired ratios of X and Y components described above. (After preparation of the compound, the Mg metal can be replaced by hydrogen, other metals, or ammonium if desired, by known methods.) The number of Mg ions in the composition is characterized by an average value of "n" of 0.1 to 1.0, and in one embodiment 0.2 or 0.4 to 0.9, and in one embodiment 0.6 to 0.8.

The salts represented by Formula (E-I) can be prepared by combining a phenol substituted by the above-described R group with formaldehyde or a source of formaldehyde (e.g., paraformaldehyde, trioxane, formalin or methal) and magnesium oxide or magnesium hydroxide under reactive conditions, in the presence of a catalytic amount of a strong base (e.g., sodium hydroxide or potassium hydroxide).

The relative molar amounts of the substituted phenol and the formaldehyde can be important in providing products with the desired structure and properties. In one embodiment, the substituted phenol and formaldehyde are reacted in equivalent ratios of 1:1 to 1:3 or 1:4, and in one embodiment 1:1.1 to 1:2.9, and in one embodiment 1:1.4 to 1:2.6, and in one embodiment 1:1.7 to 1:2.3. Thus, in one embodiment, there is a 2:1 equivalent ratio of formaldehyde to substituted phenol. (One equivalent of formaldehyde is considered to correspond to one H₂CO unit; one equivalent of phenol is considered to be one mole of phenol.) In one embodiment of the Mg species, the mole ratio of alkylphenol:formaldehyde:Mg is 1:1.4:0.4, that is, for example, (1) : (1.3 to 1.5) : (0.3 to 0.5), the amounts being the quantities actually retained in the final product, rather than the amounts charged to the reaction.

The process can be conducted by combining the above components with an appropriate amount of magnesium oxide or magnesium hydroxide with heating and stirring. A diluent such as mineral oil or other diluent oil can be included. An additional solvent such as an alcohol can be included if desired, although it is believed that the reaction may proceed more efficiently in the absence of additional solvent. The reaction can be conducted at room temperature or a slightly elevated temperature such as 35 to 120°C.

The hydrocarbon-substituted saligenin salt (E) may be overbased. When these salts are overbased, the stoichiometrically excess metal can be magnesium or it can be another metal or a mixture of cations. The basically reacting metal compounds used to make these overbased salts are usually an alkali or alkaline earth metal compound (i.e., the Group IA, IIA, and IIB metals excluding francium and radium and typically excluding rubidium, cesium and beryllium), although other basically reacting metal compounds can be used. Compounds of Ca, Ba, Mg, Na and Li, such as their hydroxides and alkoxides of lower alkanols are usually used. Overbased salts containing a mixture of ions of two or more of these metals or other cations, including mixtures of alkaline earth metals such as Mg and Ca, can be used.

The hydrocarbon-substituted saligenin salt (E) may be employed in the inventive lubricating oil composition at a concentration in the range of up to 5% by weight, and in one embodiment 0.5 to 5% percent by weight, and in one embodiment 1% to 2.5% by weight.

The following examples disclose the preparation of hydrocarbon-substituted saligenin salts that are useful in preparing the inventive lubricating oil composition. In the following examples as well as throughout the specification and claims, unless otherwise indicated, all parts and percentages are by weight and all temperatures are in degrees Celsius.

Example E-1

To a 5-L, 4-necked round bottom flask equipped with stirrer, stopper, thermowell, and reflux condenser, the following are charged: 670 g diluent oil (mineral oil), 1000 g dodecyl phenol, and a solution of 3 g NaOH in 40 g water. The mixture is heated to 35°C with stirring. When 35°C is attained, 252 g of paraformaldehyde (90%) are added to the mixture and stirring is continued. After 5 minutes, 5 g of MgO and 102 g of additional diluent oil are added. The mixture is heated to 79°C and held at temperature for 30 minutes. A second increment of 58 g MgO is added and the batch is further heated and maintained at 90-100°C for 1 hour. Thereafter the mixture is heated to 120°C under a flow of nitrogen at 28 L/Hr (1.0 std. ft³/hr.). When 120°C is reached, 252 g diluent oil is added, and the mixture is stripped at a pressure of 2.7 kPa (20 torr) at 120°C for 1 hour and then filtered. The resulting product contains 1.5% by weight magnesium and has a TBN of 63. Analysis of the product by 1D and 2D ¹H/¹³C NMR reveals an aldehyde content of 29 mole %, a methylene bridge content of 38 mole %, an ether bridge content of 12 mole %, and a hydroxymethyl content of 21 mole %.

Example E-2**Part A:**

To a 5-L, 4-necked round bottom flask equipped with stirrer, stopper, thermowell, and reflux condenser, the following are charged: 670 g diluent oil (mineral oil), and 1000 g dodecyl phenol. The mixture is heated to 35°C with stirring. When 35°C is attained, 252 g of paraformaldehyde (90%) are added to the mixture and stirring is continued. After 5 minutes, 7.3 g of Ca(OH)₂ and 102 g of additional diluent oil are added. The mixture is heated to 79°C and held at temperature for 30 minutes. A second increment of 104 g of Ca(OH)₂ is added and the batch is further heated and maintained at 90-100°C for 1 hour. Thereafter the mixture is heated to 120°C under a flow of nitrogen at 28 L/Hr (1.0 std. ft³/hr.). When 120°C is reached, 252 g diluent oil is added. The mixture is stripped under a nitrogen flow at 150°C

and isolated by filtration. The resulting product contains 14 mole % aldehyde functionality.

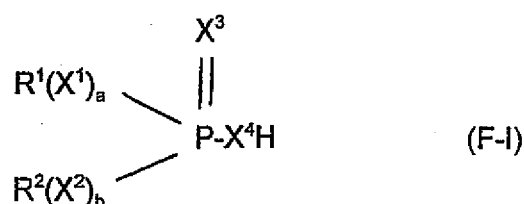
Part B:

5 Into a 12 L four-necked flask equipped with stirrer, thermowell, reflux condenser and subsurface tube is charged 5000 g of the product from Part A, 315 g of polyisobutene ($\bar{M}_n = 1000$) substituted succinic anhydride, 376 g $\text{Ca}(\text{OH})_2$ and 863 grams of an alcohol mixture containing 88-96% by weight ethyl alcohol, 4-5% by weight isopropyl alcohol and 0-8% by weight water. The mixture is heated to 63°C and 10 grams glacial acetic acid are added. The mixture is held at approximately 10 60°C for one hour. Carbon dioxide is blown through the mixture for 3 hours at approximately 0.5 std. ft³/hr. to a direct base number of 56.4. A second increment of 370 grams $\text{Ca}(\text{OH})_2$ is added and carbon dioxide is similarly blown through the mixture over seven hours to a direct base number of 39.8. The mixture is stripped to 145°C under a nitrogen flow of 1.5 std. ft³/hr. and maintained at that temperature 15 for 1 hour at 2.0 std. ft³/hr. The product is diluted with toluene, centrifuged, decanted from the resulting solids and restripped to 130-140°C and 60 mmHg vacuum. The product is filtered and exhibits a TBN of 205, containing 7.2% by weight Ca.

(F) Phosphorus-Containing Metal Salt

20 The phosphorus-containing metal salt, which typically functions as an extreme pressure (EP) additive, may be added to the inventive lubricating oil composition, provided that the amount of phosphorus contributed to the lubricating oil composition by this additive does not exceed 0.08% by weight of the lubricating oil composition, and the amount of sulfur does not exceed 0.25% by weight. The phosphorus-containing acids useful in making these EP additives may be 25 represented by the formula

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wherein in Formula (F-I): X^1 , X^2 , X^3 and X^4 are independently oxygen or sulfur, a and b are independently zero or one, and R^1 and R^2 are independently hydrocarbyl groups.

Useful phosphorus-containing acids are phosphorus- and sulfur-containing acids. These include those acids wherein in Formula (F-I) X^3 and X^4 are sulfur, X^1 and X^2 are oxygen, and a and b are each 1.

R^1 and R^2 in Formula (F-I) are independently hydrocarbyl groups that are usually free from acetylenic and ethylenic unsaturation and in one embodiment have from 1 to 50 carbon atoms, and in one embodiment from 1 to 30 carbon atoms, and in one embodiment from 3 to 18 carbon atoms, and in one embodiment from 3 to 8 carbon atoms. Each R^1 and R^2 can be the same as the other, although they may be different and either or both may be mixtures. Examples of R^1 and R^2 groups include isopropyl, n-butyl, isobutyl, amyl, 4-methyl-2-pentyl, isooctyl, decyl, dodecyl, tetradecyl, 2-pentenyl, dodecenyl, phenyl, naphthyl, alkylphenyl, alkylphenyl, phenylalkyl, naphthylalkyl, alkylphenylalkyl, alkylphenylalkyl, and mixtures thereof. Particular examples of useful mixtures include, for example, isopropyl/n-butyl; isopropyl/secondary butyl; isopropyl/4-methyl-2-pentyl; isopropyl/2-ethyl-1-hexyl; isopropyl/isooctyl; isopropyl/decyl; isopropyl/dodecyl; and isopropyl/tridecyl.

In one embodiment, the phosphorus-containing compound represented by formula (F-1) is a compound where a and b are each 1, X^1 and X^2 are each O, and R^1 and R^2 are derived from one or more primary alcohols, one or more secondary alcohols, or a mixture of at least one primary alcohol and at least one secondary alcohol. Examples of useful alcohol mixtures include: isopropyl alcohol and isoamyl alcohol; isopropyl alcohol and isooctyl alcohol; secondary butyl alcohol and isooctyl

alcohol; n-butyl alcohol and n-octyl alcohol; n-pentyl alcohol and 2-ethyl-1-hexyl alcohol; isobutyl alcohol and n-hexyl alcohol; isobutyl alcohol and isoamyl alcohol; isopropyl alcohol and 2-methyl-4-pentyl alcohol; isopropyl alcohol and sec-butyl alcohol; isopropyl alcohol and isooctyl alcohol; isopropyl alcohol, n-hexyl alcohol and isooctyl alcohol, etc. These include a mixture of 40 to 60 mole % 4-methyl-2-pentyl alcohol and 60 to 40 mole % isopropyl alcohol; a mixture of 40 mole % isooctyl alcohol and 60 mole % isopropyl alcohol; a mixture of 40 mole % 2-ethylhexyl alcohol and 60 mole % isopropyl alcohol; and a mixture of 35 mole % primary amyl alcohol and 65 mole % isobutyl alcohol.

The metal salts of the phosphorus-containing acids represented by Formula (F-I) which are useful include those salts containing Group IA, IIA or IIB metals, aluminum, lead, tin, iron, molybdenum, manganese, cobalt, nickel or bismuth. Zinc is a useful metal. These salts can be neutral salts or overbased salts.

The phosphorus-containing metal salt (F) may be employed in the inventive lubricating oil composition at a concentration in the range of up to 2.5% by weight, and in one embodiment 0.1 to 2.5% percent by weight, and in one embodiment 0.2% to 2% by weight, and in one embodiment 0.2 to 1.5% by weight.

(G) Dispersant Viscosity Index Modifier

The dispersant viscosity index modifier (G) is a multifunctional additive that provides both viscosity improving properties and dispersant properties. These additives are known in the art and are commercially available.

The dispersant viscosity index modifiers typically comprise an oil soluble polymeric hydrocarbon backbone having a weight average molecular weight greater than 20,000, and in one embodiment from 20,000 to 500,000 or greater. In general, these dispersant viscosity index modifiers are functionalized polymers. For example the dispersant viscosity index modifier may be an olefin copolymer (e.g., an interpolymer of ethylene-propylene) or an acrylate or methacrylate copolymer that is grafted with an active monomer such as maleic anhydride and then derivatized with, for example, an alcohol or amine.

Derivatives of polyacrylate esters are well-known as dispersant viscosity index modifiers. Dispersant acrylate or polymethacrylate viscosity modifiers are useful.

The dispersant viscosity index modifier (G) may be employed in the inventive lubricating oil composition at a concentration in the range of up to 10% by weight, and in one embodiment up to 4% by weight, and in one embodiment 0.5 to 4% percent by weight, and in one embodiment 0.5% to 3% by weight. .

(H) Other Optional Additives

The inventive lubricating oil composition may contain, in addition to the acylated nitrogen-containing compounds (C) and the dispersant viscosity index modifiers (G) referred to above, one or more detergents or dispersants of the ashless type.

The inventive lubricating oil composition may also contain other lubricant additives known in the art. These include, for example, corrosion-inhibiting agents, antioxidants, viscosity modifiers, pour point depressants, friction modifiers, fluidity modifiers, copper passivators, anti-foam agents, etc.

Each of the foregoing additives, when used, is used at a functionally effective amount to impart the desired properties to the lubricant. Generally, the concentration of each of these additives, when used, ranges from 0.001% to 20% by weight, and in one embodiment 0.01% to 10% by weight based on the total weight of the lubricating oil composition.

The additives (B) through (H) can be added directly to the lubricating oil composition. In one embodiment, however, they are diluted with a substantially inert, normally liquid organic diluent such as mineral oil, synthetic oil, naphtha, alkylated (e.g., C₁₀-C₁₃ alkyl) benzene, toluene or xylene to form an additive concentrate. These concentrates usually contain from 1% to 99% by weight, and in one embodiment 10% to 90% by weight of such diluent.

Examples

The following Examples 1 and 2 are provided to further disclose the invention. Example C-1 is not within the scope of the invention, but is provided for purposes of comparison. Each example consists of a lubricating oil composition which is disclosed in the table below. In the table below, all numerical values relating to the ingredients (except of the antifoam agent) of each exemplified lubricating oil composition are in percent by weight of the composition. The antifoam agent concentration is expressed in parts per million weight. The exemplified lubricating oil compositions are tested using one or more of the following tests and the results of such tests are also reported in the table below.

Motorized Valve Train Wear Test

The motorized valve train wear test uses a full-scale cylinder head driven by an electric AC motor and operated by a Camille data acquisition and control computer system. The test sequence consists of 100, one hour cycles with two stages in each cycle. Stage one is run for fifty minutes at 800 rpm. Stage two is run for ten minutes at 1500. The oil sample is contaminated by an oxidizing agent, water, and fuel. Wear measurements are conducted by measuring all 12 cam lobes. Wear is expressed in microns of lost material.

Screen Valve Train Wear Test

This test uses a CH-4 Cummins M-11 diesel engine to determine heavy duty diesel valve train wear performance. The CH-4 Cummins M-11 is a turbocharged in-line 6 cylinder, 11 liter engine. The engine test is broken into four stages. During the first and third stage, the engine is over-fueled and is operated with retarded timing to generate soot at an accelerated state. The second and fourth stages are run at a lower speed and higher torque to induce wear.

	C-1	1	2
Base Oil: 90% 200N mineral oil + 10% 100N mineral oil	79.14	78.25	78.47

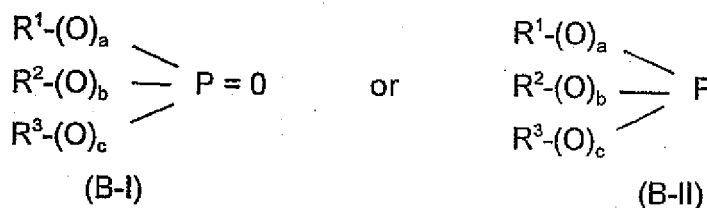
		C-1	1	2
	Viscosity modifier: LZ 7095D available from Lubrizol identified as olefin polymer dispersed in oil (89% diluent oil)	8.2	8.2	8.2
5	Pour point depressant: Styrene-maleic anhydride copolymer dispersed in oil (53.6% diluent oil)	0.20	0.20	0.20
10	Dispersant: succinimide dispersant derived from polyisobutene ($M_n=2000$) substituted succinic anhydride and polyethylene amines dispersed in oil TBN = 27, nitrogen content = 1.16% (50% diluent oil)	7.2	7.2	7.2
	Detergent: calcium sulfonate dispersed in oil, TBN = 85 (47% diluent oil)	0.38	0.38	0.38
15	Detergent: calcium sulfonate dispersed in oil, TBN = 300 (42% diluent oil)	2.05	2.05	2.05
	Detergent: Product of Example E-1	1.31	1.31	1.31
	Antioxidant: hindered phenolic C_4 ester	0.4	0.4	0.4
	Antioxidant: Nonylated diphenyl amine	0.2	0.2	0.2
20	Antiwear: Durad 310M (product of FMC identified as tri (alkyl phenol) phosphate)	—	0.89	—
	Antiwear: triphenyl phosphite	—	—	0.67
	EP Additive: zinc dialkyl dithiophosphate dispersed in oil, TBN=5 (9% diluent oil)	0.5	0.5	0.5
25	Copper passivator: 1,3,4-thiadiazole-2,5-bis (tert-nonyl dithio) having a nitrogen content of 6.4%	0.03	0.03	0.03
	Diluent oil	0.39	0.39	0.39
	Antifoam: polydimethylsiloxane dispersed in oil (90% diluent oil)	100ppm	100ppm	100ppm

	C-1	1	2
Chemical analysis:			
Phosphorous, %	0.05	0.115	0.115
Sulfur, %	0.17	0.17	0.17
Magnesium, ppm	200	200	200
Ash content, %	1.08	1.05	1.05
Motorized Valve Train Wear Test, microns	161	39	29
Screen Valve Train Wear Test, mg.	8.57	4.1	—

While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such modifications as fall within the scope of the appended claims.

Claims

1. A lubricating oil composition, comprising:
- (A) a base oil; and
- (B) a phosphorus-containing compound represented by the formulae



wherein in Formulae (B-I) and (B-II), R^1 , R^2 and R^3 are independently hydrogen or hydrocarbyl groups, and a , b and c are independently zero or 1;

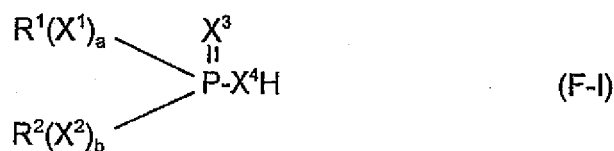
the lubricating oil composition being characterized by a sulfur content of 0.01 to 0.25% by weight.

2. The composition of claim 1 wherein the composition further comprises (C) an acylated nitrogen-containing compound having a substituent of at least 10 aliphatic carbon atoms.

3. The composition of claim 1 wherein the composition further comprises (D) an alkali or alkaline earth metal salt of an organic sulfur acid, a carboxylic acid, a lactone or a phenol.

4. The composition of claim 1 wherein the composition further comprises (E) an alkali or alkaline earth metal salt of a hydrocarbon-substituted saligenin.

5. The composition of claim 1 wherein the lubricating composition further comprises (F) a metal salt of a phosphorus-containing compound represented by the formula



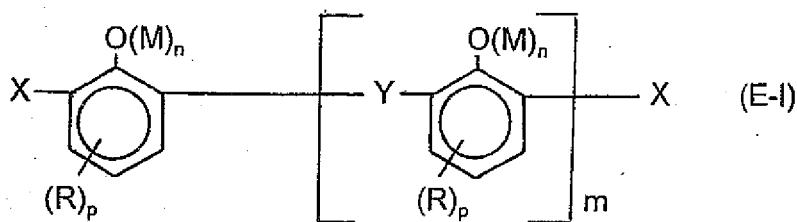
wherein in Formula (F-I), X^1 , X^2 , X^3 and X^4 are independently O or S; a and b are independently zero or 1; and R^1 and R^2 are independently hydrocarbyl groups.

6. The composition of claim 1 wherein the lubricating oil composition further comprises (G) a dispersant viscosity index modifier.

7. The composition of claim 1 wherein in Formula (B-I), R^1 , R^2 and R^3 are independently aromatic or alkyl aromatic groups, and a, b and c are each 1.

8. The composition of claim 1 wherein (B) is a tri (alkylphenol) phosphate or a triphenyl phosphite.

9. The composition of claim 4 wherein (E) is a compound represented by the formula



wherein in Formula (E-I): each X independently is -CHO or -CH₂OH; each Y independently is -CH₂- or -CH₂OCH₂-; wherein the -CHO groups comprise at least 10

5 mole percent of the X and Y groups; each M is independently the valence of an alkali or alkaline earth metal ion; each R is independently a hydrocarbyl group containing 1 to 60 carbon atoms; m is 0 to 10; n is 0 or 1 provided that when n is 0 the M is replaced with H; and each p is independently 0, 1, 2, or 3; provided that at least one aromatic ring contains an R substituent and that the total number of carbon atoms in all R groups is at least 7; and further provided that if m is 1 or greater, then one of the X groups can be -H.

10 10. The composition of claim 1 wherein the lubricating oil composition further comprises at least one ashless detergent or dispersant, corrosion-inhibiting agent, antioxidant, viscosity modifier, pour point depressant, friction modifier, fluidity modifier, copper passivator or anti-foam agent.